



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE ACCURACY OF THE IMPROVED VOLTAMETER.

BY THEODORE WILLIAM RICHARDS AND GEORGE WILLIAM HEIMROD.

Presented February 12, 1902. Received January 29, 1902.

INTRODUCTION.

IN a recent preliminary paper * it was shown that the disturbing influences in the common silver "voltameter" (or better, *coulometer* †) are due to the concentrated liquid which falls from the anode. In order to avoid the inaccuracy thus caused, it was suggested that the anode be surrounded by a fine-grained porous cup, which is capable of preventing this heavy liquid from reaching the kathode.

The weight of silver deposited by a given current in such a voltameter was found to correspond very closely to the amount of copper deposited at the same time in a copper voltameter shielded as much as possible from all discoverable sources of error; hence it seemed probable that the new voltameter gives the true value of the electrochemical equivalent of silver.

In a matter so important as this, however, it seemed advisable to obtain much more information concerning the constancy and trustworthiness of the new instrument, as well as to discover if possible the mechanism of the phenomena which rendered the older form untrustworthy. The investigation described below was undertaken with these objects.

I. THE CONSTANCY OF THE POROUS CUP VOLTAMETER.

The first problem was to determine if two instruments in series would always give identical results; in other words, to find if the new voltameter is always consistent with itself.

* Richards, Collins, and Heimrod, These Proceedings, **35**, 123 (1899).

† The word "voltameter" was devised before electrical dimensions were understood. It is moreover too much like the universally used and suitable word "voltmeter." Now that the former instrument is placed upon a firm basis of accuracy, it may appropriately receive also an accurate name; and it is hoped that the new word "coulometer" may replace wholly the anachronism.

Nine such duplicate experiments were made. The first of these was a crude trial, and need not be recorded; the eight others are given in the following table.

The apparatus employed was precisely like that described in the previous paper. For the sake of easy reference, the description is repeated below.

Small cylinders of Pukal's porous ware (Berlin), suitable for osmotic pressure experiments, were used to enclose the anode in order to prevent the heavy anode-solution from reaching the kathode. These vessels

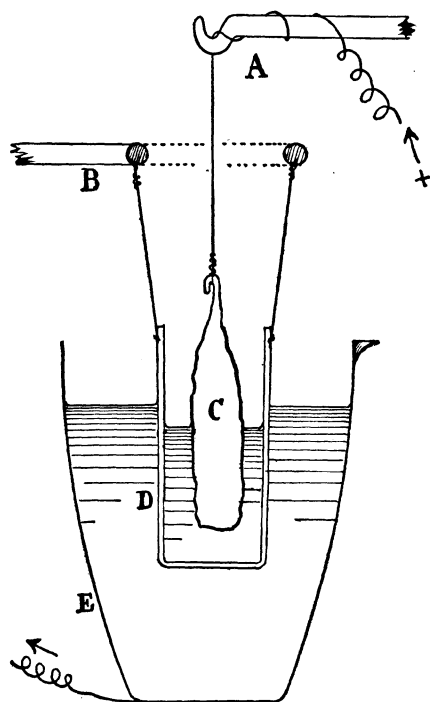


FIGURE 1. — POROUS CUP VOLTAMETER
($\frac{2}{3}$ actual size).

A, glass hook for supporting anode. B, glass ring for supporting porous cup. C, silver anode. D, porous cup. E, platinum kathode.

were 50 millimeters high and 20 in diameter; their walls were not much over one millimeter in thickness. Their impurities were removed by boiling with nitric acid and thorough washing with water. Before being used they should be carefully searched and tested for cracks or imperfections. They were suspended in the solution by means of a platinum wire hung upon a glass hook, which insulated the wire from the electric connections. By means of a siphon, or a small pipette with a rubber top, the liquid within the cup was always kept at a lower level than that without, so as to prevent outward filtration.

The kathodes consisted of large crucibles weighing only 60 grams, although they were capable of holding 120 cubic centimeters; they were provided with lips. A crucible exposes a smaller surface of

liquid to the impurities of the atmosphere, and gave in our experiments a more evenly distributed deposit than a bowl.

The anodes were bars $5 \times 1 \times 1$ centimeters of the purest silver, supported by silver wires and not enclosed in filter paper; and the electrolyte usually contained ten grams of pure, freshly prepared argentic nitrate in a hundred cubic centimeters of solution.

The manipulation was simple. The platinum crucibles were cleaned, dried at 160° , and weighed after three or four hours' cooling in a large desiccator kept in the balance-room. In order to prevent leakage during the electrolysis, the several stands were insulated by separate glass plates, and all the connections were air lines. The apparatus was protected, as in the earlier experiments with copper, by a miniature house with walls of fine cotton cloth, which helped to exclude dust. When the current was broken, the electrolyte was removed, the silver was rinsed twice with water, a third filling with water was allowed to stand in the crucible for two or three hours, and a fourth one remained in it over night. The wash-waters were collected and filtered if the silver showed any tendency to break off. In such cases a Gooch crucible was employed to collect the particles; and a very small filter, afterwards burned, served to catch the minute flakes of asbestos detached from the mat. On the next morning the crucibles were washed once more, rinsed twice with pure alcohol, and finally dried and weighed as before. This method of treatment gave opportunity for the diffusion of mother liquor from the intricate recesses of the crystallized mass, while it did not run the risk of dissolving silver which may attend the use of boiling water for washing.

As has been said, the crucibles were dried at 160° . It was subsequently shown, in agreement with the results of Lord Rayleigh and Mrs. Sidgwick, that a red heat is needed to drive off all the included liquid from the silver crystals; but since the amount included is fairly constant, this fact does not interfere with the availability of the uncorrected data for the present purpose of comparing one weight of silver with another.

Weighings were made upon the balance which served for the weighings in the earlier work upon copper, — one which has served also for many determinations of atomic weights. Its results with small objects may be depended upon to within $\frac{1}{80}$ milligram. All weighings were made by double substitutions, a similar vessel being used as a tare, and the weights were of course carefully standardized. Since the question concerned merely the comparison of silver with silver, the results were not at first corrected to the vacuum standard.

The results show that the average difference between the weights of the silver deposited in two crucibles placed in series was less than the tenth of a milligram, or only about four parts in one hundred thousand.

Considering the size of the platinum vessels weighed, this average agreement is all that could be expected; hence the test of the constancy of the apparatus seems to have been satisfactory.

TABLE I.

TEST OF THE CONSTANCY OF THE POROUS CUP VOLTAMETER.

No. of Experiment.	Voltameter I. Weight of Silver.	Voltameter II. Weight of Silver.	Difference.	Percentage Difference.
	grams.	grams.	milligram.	per cent.
2	2.43744	2.43749	0.05	0.002
3	2.69691	2.69713	0.22	0.008
4	2.36193	2.36196	0.03	0.001
5	2.14900	2.14913	0.13	0.006
6	1.65485	1.65490	0.05	0.003
7	2.31480	2.31500	0.20	0.009
8	2.22258	2.22260	0.02	0.001
9	2.67264	2.67268	0.04	0.002
Mean difference 0.09				0.004

There is of course nothing in this table to show whether the figures represent the weight of silver which ought to have been deposited by the quantities of electricity employed. It may be that the error of the old voltameter was merely reduced, and that a small constant error still remained. The most probable cause of such a remaining error seemed to be the possible diffusion or migration of the heavy anode-liquid through the bottom of the porous cup, in spite of the fact that it was continually removed by means of a pipette or siphon. In order to prevent this, the bottom and a few millimeters of the sides of a porous cup were filled with melted paraffin, which effectually sealed the pores. The upper part of the sides only served to allow the passage of the electricity. A tenth comparison showed that a current which deposited 1.83370 grams of silver in this cup deposited 1.83375 grams in the ordinary porous cup coulometer. This difference is no greater than a possible experimental error; hence we may conclude that the effect of the diffusion is imperceptible. It will be shown later that the substance which causes the chief

irregularity of Lord Rayleigh's voltameter is probably a heavy complex ion; hence it is not surprising that both the migration-rate and the diffusion-rate of the impurity is small. On the other hand, when the porous cup is too coarse-grained or too large, or when the anode solution is allowed to rise too high and thus filter through, the effect of the diffusion begins to be manifest. The same error begins to show itself when the viscosity of the solution is diminished by increasing temperature, as we showed in the preceding paper.

If now the formation of ionized silver at the anode is attended by such disturbing side reactions, it is reasonable to assume that a remedy may be found in the use of an anode of some other metal. For this purpose zinc seemed to offer peculiar advantages; it possesses only one degree of quantivalence, and has so great a solution-tension as to avoid the possibility of contaminating the deposit of silver at the kathode.

A zinc rod (so-called "C. P.") served as the anode in the following two experiments, and it was surrounded by a ten per cent solution of zincic nitrate prepared from the same material by solution in nitric acid (standing for a week over zinc), filtration, and crystallization. The kathode solution consisted of a ten per cent solution of argentic nitrate, as usual.

TABLE II.
THE EFFECT OF A ZINC ANODE.

No. of Experiment.	Wt. of Silver in Ordinary Porous Cup Voltameter.	Wt. of Silver in Voltameter with Zinc Anode.	Difference.	Percentage Difference.
	grams.	grams.	milligram.	per cent.
11	2.69702	2.69688	-0.14	-0.005
12	2.36195	2.36209	+0.15	+0.006
Average error				0.001

A peculiar reaction was observed during this electrolysis. The zinc rod was covered with a copious white flaky precipitate, and a marked test for nitrite was observed in the supernatant solution.* Thus the ionization of the zinc is attended with the formation of basic salt and

* See also Senderens, *Comp. Rend.*, **104**, 504; also *Ber. d. d. ch. Ges.*, **20**, 197 R (1887).

zinc nitrite. The NO_3' ion must have been decomposed into NO_2' and oxygen. This same reaction takes place when silver serves as an anode in its nitrate solution, although to a much smaller extent.

In spite of the irregularities just described, the deposition on the cathode proceeded in a perfectly regular manner, and the figures show that as much silver was deposited in one cell as in the other.

Still another means of testing the porous cup voltameter was found in its comparison with a device which eliminates the porous cup wholly, but which nevertheless keeps the anode solution quite away from the cathode. This device consists in placing the anode at the bottom of a tall beaker filled with a concentrated solution of argentic nitrate (200 grams of the salt in a litre of solution), and arranging the cathode in the upper part of the vessel.* The anode solution becomes heavier and remains around the anode, while the cathode solution becomes lighter and rises to the surface. In order to prevent this dilution around the cathode from diminishing too much the concentration of the contiguous liquid, it is well to sink the cathode at least two centimeters below the surface. A circular disk of platinum wire gauze,† six centimeters in diameter, was used as the cathode, since many holes in gauze permitted the ready escape upward of the impoverished electrolyte. The gauze was bent around a stout circular platinum wire, and the disk was stiffened by four radial wires, and was hung rigidly from the centre. The vertical distance between this cathode and the anode was about seven centimeters. The anode consisted of a plate of pure silver, and its platinum connecting wire was protected from the solution by an enclosing glass tube.

The chief trouble encountered in manipulating the voltameter thus constructed is the danger of losing fine crystals of silver from the flexible gauze. In the two experiments described below every precaution was taken to avoid this source of error, and it is believed that no appreciable weight was lost. Another disadvantage of the gauze is the fact that metals deposited upon it are very apt to include minute quantities of electrolyte because of the interstices arising from its woven structure. Even silver deposited in a crucible contains some included mother liquor, and that deposited on the gauze contains much more. In the two experiments given below, the first deposit on the gauze lost 0.42 milligram on gentle ignition in a large porcelain crucible, and the

* Merrill, *Phys. Rev.*, X, 169 (1900).

† Paweck, *Zeitsch. für Berg. u. Hüttenwesen*, **46**, 570 (1898); Winkler, *Ber. d. d. ch. Ges.*, **32**, 2192 (1899).

second lost 0.72 milligram, while the two crucible deposits lost respectively 0.20 and 0.24 milligram. These losses, accompanied by audible decrepitation, must have been due to retained electrolyte.

In the table the weights of the ignited precipitates are given.

TABLE III.

COMPARISON OF POROUS CUP VOLTAMETER WITH WIRE GAUZE VOLTAMETER.

No. of Experiment.	Weight of Silver in Porous Cup Voltameter.	Weight of Silver deposited on Gauze.	Difference.	Percentage Difference.
	grams.	grams.	milligram.	per cent.
13	2.10326	2.10344	+0.18	+0.009
14	2.31237	2.31234	−0.03	−0.001
Average error +0.03				+0.004

The gauze kathode thus showed an average surplus of less than a tenth of a milligram. But even this slight error is explicable, for it is clear that the argentic nitrate held by the electrolyte must have left silver nitrite or silver behind on heating. If we assume that the temperature of ignition was enough wholly to decompose the electrolyte, the average loss of 0.57 milligram would correspond to a residue of about 0.1 milligram, while the corresponding residue from the weaker solution used in the porous cup voltameter could not have exceeded 0.02 milligram. The difference between these two figures is exactly equal to the observed difference between the gauze voltameter and the porous cup voltameter, so that the two may be said to give precisely identical results.

An important point connected with this experiment is the fact that the kathode surface available for deposition on the gauze had an area of less than half that on the inside of the large crucible. Hence the current density in the gauze voltameter must have been over twice that in the standard.

There has thus been accumulated a convincing array of evidence indicating that the porous cup voltameter affords a means of depositing the amount of silver which really corresponds to the quantity of electricity sent through it. The numerical averages may be summed up in a brief table as follows : —

Average deviation of two porous cup voltmeters in series	=	$\pm \frac{4}{100,000}$
Difference caused by sealing bottom of cup	=	$-\frac{3}{100,000}$
Difference caused by use of zinc anode	=	$\pm \frac{1}{100,000}$
Difference (corrected) between gauze voltmeter and cup voltmeter		± 0

The agreement of these results is as close as could be expected, since the discrepancies do not exceed the possible experimental error. With Lord Rayleigh's method, when two precisely similar voltmeters are compared, Kahle* and Rodger and Watson† have shown that an accuracy of 6 or 7 parts in 100,000 can be obtained. On the other hand, the least variation of size of kathode or anode, or of any other condition, causes large deviations which may amount to ten times as large an error. In our experiments given above, the most radical changes of method were introduced, without affecting the results.

Among the efficient forms of apparatus described above, the porous cup voltmeter with a silver anode is the most convenient. Hence for the further purposes of this paper it will be chosen as the standard method.

II. THE SEPARATE EFFECT OF EACH ANODE IRREGULARITY.

It is obvious from the study of earlier work that more than one irregularity exists at the anode in a silver cell; and the separation and identification of the individual effect of each irregularity became a matter of considerable interest. The outcome was instructive as an example of the multitude of hidden minor influences which so often modify the obvious outcome of chemical experiment.

Qualitative testing revealed not only acid, but also nitrite, in the anode liquid; and in those cases where the anode is very small, some experimenters have indicated the formation of highly oxidized compounds of silver. Moreover, the singular crystalline silver dust which forms around the anode demands an explanation. In order to solve the problem, of course an obvious available method was to introduce artificially each impurity in turn into the pure liquid around the kathode in the porous cup voltmeter, and study its effect on the gain in weight of the kathode.

The first impurity to be investigated was the nitrite. In order to pre-

* Wied. Ann. N. F., **67**, 22 (1899).

† Phil. Trans., **186 A**, 633 (1895).

pare the nitrite, we had recourse at first to a method used by Proust.* He has found that on boiling an argentic *nitrate* solution with finely divided silver, the *nitrite* is produced in quantity. In repeating this experiment, powdered silver reduced from purest silver chloride by the Stas method was boiled in a ten per cent argentic nitrate solution. Nitrite was indeed formed, but a very fine film of crystallized metallic silver was formed on the surface; a complication which seemed to point towards the existence of a reaction similar to the solution of copper in cupric sulphate. But it was found that pure silver nitrite in neutral silver nitrate solution likewise deposits a fine silver mirror on exposure to the light; hence the silver in both cases must be supposed to result simply from the decomposition of the nitrite. The solution boiled with silver was filtered through a Gooch crucible, and after cooling was employed in a voltameter with a porous cup. The solution containing the nitrite deposited 2.27945 grams of silver, while pure argentic nitrate in another standard voltameter deposited 2.27944 grams, a difference of only 0.01 milligram. (Exp. 15.)

Evidently the nitrite present had no effect at the kathode; and the liquid in an ordinary voltameter could hardly contain more nitrite than this solution which had been boiled with metallic silver. In order to pursue the matter further, however, we prepared silver nitrite from pure potassium nitrite and silver nitrate.† Pure potassic hydrate was neutralized with nitric acid; the nitrate was re-crystallized and fused in a silver crucible, and the resulting mixture of nitrate and nitrite was extracted

TABLE IV.

STANDARD *vs.* VOLTAMETER WITH SOLUTION SATURATED WITH AgNO_2 .

No. of Experiment.	Type of Voltameter containing Nitrite.	Weight of Silver in Standard.	Weight of Silver in Voltameter containing AgNO_2 .	Difference.	Percentage Difference.
		grams.	grams.	milligrams.	per cent.
16	Standard.	2.27944	2.28011	0.67	0.030
17	Filter paper volt.	2.30276	2.30539	2.63	0.114

* Journ. de Physique, March, 1806, 211; also Nicholson's Journal, **15**: 378.

This reference has evidently been lost, since no text-book, including Dammmer, gives it, although all mention Proust's observation. After a long search through the journals published in Proust's days, the reference was rediscovered.

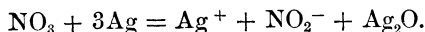
† Victor Meyer, Liebig's Ann., **171**, 23 (1874).

with boiling water. The great bulk of nitrate may then be removed by one crystallization. If to the mother liquor is added a solution of argentic nitrate, the argentic nitrite will precipitate at once as a thick yellow paste. This is washed and re-crystallized from hot water, until the color has changed to white. The pure nitrite was dissolved in a nitrate solution to saturation, and this was employed, *first*, with a porous cup (16), and *second*, with a paper-wrapped anode (17).

The results show that a saturated solution of nitrite really has the effect of increasing the kathode deposit.

Since the increase due to a paper-wrapped anode over the weight found with a porous cup would have been from 0.04 to 0.08 per cent, the nitrite caused an increase of about the same amount in each case. But this increase happens only when the solution is *saturated* with nitrite; hence it is interesting chiefly as a limiting effect, and can hardly be important in solutions of nitrite as dilute as those formed spontaneously around the anode. The formation of nitrite is evidently the result of the breaking-up of the NO_3^- ion into the nitrite ion NO_2^- and oxygen, and the latter is probably taken up by the silver in forming one of the oxidized compounds to be discussed later.

It is not at all surprising that this side reaction should take place to a small extent. The current is normally carried from the anode to the solution by the formation of the silver ion from the metal; but a slight tardiness in this reaction (which might be named "physico-chemical inertia") would result in assistance from the anions in the neighborhood. They would seek to adjust the potential by discharging their negative electricity on the anode. Of course the most plentiful anion in the vicinity is the nitrate ion; its deionization would make possible the formation of the *nitrite* ion and oxygen, which might at once oxidize the silver plentifully present.* The reaction might be written thus: —



Thus the electrolysis of a strong solution of argentic nitrate might be predicted to result in the neutralization of a previously acid solution — a prediction which agrees with the fact discovered by Rodger and Watson† with thirty per cent solutions of argentic nitrate. It is possible that a higher oxide also would be found if the anode were small.

* The probable presence of silver in supersaturated solution around the anode will be shown later.

† Rodger and Watson, Phil. Trans., **186 A**, 631 (1895).

But Kahle* found that in weaker solutions acid is produced instead of being removed, and we have verified his results. Clearly this must be due to yet another irregularity. When the solution is dilute and neutral, oxygen and hydroxyl ions are both present in appreciable amount, according to modern electrochemical interpretation. Their greater ease of deionization would compensate for their relatively small concentration, and traces of negative electricity might be carried out of the solution through their agency with the formation again of argentic oxide, or even oxygen gas. The reaction would, however, leave an excess of ionized hydrogen (acid) in solution, a state of affairs not paralleled in the case of the nitrite. This would explain the phenomena in question.

But would not the argentic oxide at once dissolve in the simultaneously formed acid, and thus form argentic nitrate again? Or, in other words, does argentic oxide form with silver an oxide-complex of any degree of stability? Hellwig† in a recent paper has shown that the weak silver ion in the presence of the strong NO_3^- ion tends to strengthen itself by taking up a molecule of some other undissociated substance, as AgCl , AgI , AgBr , or AgCN . He has proved also that the solution actually contains ions like Ag_2I^+ , since on electrolysis the iodine accumulates at the kathode, and disappears from the anode.

In order to find if argentic oxide could in a similar way associate itself with the silver ion, we boiled very pure argentic oxide with a concentrated solution of argentic nitrate, and filtered the solution hot. Upon being diluted with cold water this solution yielded a white precipitate, which turned gray upon standing. The precipitate was soluble in dilute nitric acid, hence it could not have been an argentic halide; besides, every precaution had been taken to exclude the halogens. The compound precipitated on dilution must, therefore, be silver hydroxide or a basic salt; and a basic complex must have existed in solution.

It is by no means inconceivable that this complex, although finally decomposed by acid, should not yield at once to its action. In the meantime the acid, diffusing at a far more rapid rate than the heavy complex, would have partly left the immediate neighborhood of the anode, and hence the heavy solution around the latter would fall with its basic load to the bottom of the kathode vessel. There the complex ion (possibly Ag_3O^+) would be capable of transferring electricity as well as any other ion, and upon deionization would deposit over three times the weight of material

* Kahle, Wied. Ann., **67**, 1 (1899).

† Zeitschr. anorg. Chem., **25**, 157 (1900).

contained in the silver ion carrying the same quantity of electricity. Part of this material would be in the form of oxide, and would therefore cause dark spots on the surface of the kathode,—spots which have actually been noticed by other experimenters.

This interpretation serves to explain also the very high results obtained by Lord Rayleigh in the presence of argentic acetate. The possibility of forming slightly dissociated acetic acid would prevent any considerable accumulation of ionized hydrogen, and the oxide-complex would grow in concentration without hindrance. This explanation seems more plausible than the provisional one suggested by Lord Rayleigh,—namely, that the acetate itself might be carried down with the silver.

In order to submit these interpretations to the test of experiment, electrolyses were conducted with solutions saturated with argentic oxide. Kahle, Patterson and Guthe, and others, have likewise carried out such electrolyses, showing that the deposit is as a matter of fact too great; but our trial is easier to interpret, because by means of the porous cup all anode complications were excluded, and the result of experiment gives the effect of argentic oxide alone.

Three trials were made, in which a given current of 0.25 ampere as usual was run first through a standard porous cup voltmeter, and then through a cell precisely similar except that the kathode solution in the latter was saturated with the argentic oxide. The following table contains the results:—

TABLE V.

STANDARD *vs.* STANDARD SATURATED WITH Ag_2O .

No. of Experiment.	Weight of Silver in Standard.	Weight of Ag Standard with Ag_2O .	Difference.	Percentage Difference.
	grams.	grams.	milligrams.	per cent.
18	2.30276	2.30449	1.73	0.075
19	2.34799	2.34887	0.88	0.037
20	2.21379	2.21489	1.10	0.050
Mean				0.055

The solution after boiling with silver oxide thus really contains, therefore, some ion heavier than Ag^+ . Since this has been formed directly

from the oxide, it probably contains Ag_2O , and may be assumed to have the formula already given, Ag_3O^+ . Thus the preceding interpretation is confirmed.

The next question which arises concerns the permanence of this complex in the presence of acid. In order to test this, a solution of argentic nitrate was saturated with argentic oxide, and then treated with a slight excess of nitric acid. After a short time, perhaps an hour, electrolyses were made with this solution in series with the standard, as usual.

TABLE VI.

STANDARD vs. STANDARD SATURATED WITH Ag_2O , BUT AFTERWARDS ACIDIFIED.

No. of Experiment.	Weight of Ag in Standard.	Weight Ag from Sol. with $\text{Ag}_2\text{O} + \text{HNO}_3$.	Difference.	Percentage Difference.
	grams.	grams.	milligrams.	per cent.
21	2.34799	2.34836	+0.37	+0.016
22	2.21379	2.21361	−0.18	−0.008

The results are somewhat less regular than usual, but clearly most if not all of the oxide-complex had been removed by the acid. Thus, while the complex is capable of existence in a neutral solution, the speed of its reaction with acid results in its decomposition in a short time, as would be expected.

It is possible that this oxide-complex is not the only one capable of being formed at the anode. Kahle, Sulc,* Mulder and Heringa† and others, present evidence showing that with a small anode, where both silver and nitrate ions would be less available for transferring electricity, a highly oxidized compound having some such formula as $\text{Ag}_7\text{NO}_{11}$ may be formed. This compound is capable of dissolving in acids, forming a brown solution; and it may be responsible for the colored rings which Kahle has noticed from old acid solutions. The fact that after boiling with metallic silver such solutions cease to yield colored rings is evidence that the foreign compound is a highly oxidized substance.

In spite of the fact that the nitrite, the oxide-complex, and the per-

* Sulc, Z. anorg. Chem., **12**, 89, 180 (1896) ; **24**, 305 (1900).

† Mulder and Heringa, Ber d. d. ch. Ges., **29**⁴, 583 (1896).

oxide-complex, may explain many of the irregularities observed during the electrolysis, they cannot explain them all. The chief questions remaining to be answered concern the cause of the high results which are still to be obtained when all the preceding causes of irregularity have been eliminated, as well as the mechanism of the formation of the plentiful "anode dust."

A number of facts point to the conclusion that some other complex compound exists in the electrolyzed liquid which is capable of depositing metallic silver upon a silver surface. Among others is the well known fact that a pure silver kathode receives a larger deposit with a given current than a platinum kathode in the old Lord Rayleigh voltameter. It seemed to be worth while to test once more this relation, in order to confirm the results of Lord Rayleigh, Kahle, and others, and also to discover if a pure argentic nitrate solution in the porous cup voltameter would give like results. The following tables record the results of our experiments. In the first place we repeated Kahle's experiments, using an anode protected only by filter paper.

TABLE VII.
FILTER PAPER VOLTAMETER ON PLATINUM AND ON SILVER.

No. of Experiment.	Weight of Deposit on Platinum.	Weight of Deposit on Silver.	Difference.	Percentage Difference.	Weight of Anode.
	grams.	grams.	milligram.	per cent.	grams.
23	2.26680	2.26672	-0.08	-0.003	2
24	2.17215	2.17250	+0.35	+0.016	4.5
25	2.18071	2.18100	+0.29	+0.013	6.7
26	2.11134	2.11162	+0.28	+0.013	8.8
Mean					+0.010

There is an undeniable surplus when the deposit is made on silver. The main question now arises, — Is this effect due to the anode solution, or is it an irregularity which would come equally from pure argentic nitrate? The answer to the question is easily determined by means of our porous cup; a comparison of deposits made in a standard voltameter on a silver and a platinum kathode gave the following results:—

TABLE VIII.

STANDARD METHOD ON PLATINUM AND ON SILVER.

No. of Experiment.	Weight of Deposit on Platinum.	Weight of Deposit on Silver.	Difference.	Percentage Difference.
	grams.	grams.	milligram.	per cent.
27	2.69700	2.69674	0.26	-0.009
28	2.25769	2.25770	0.01	+0.000

The only difference is now in the opposite direction ; and this was due to known experimental error.. In experiment 27 a small loss of silver particles in the wash-water from the silver cell produced the difference of 0.009 per cent. It is highly probable that but for this accident, the deposit on silver would have been equal to that on platinum, as it is in No. 28. These results permit us to draw two conclusions. First, it is not the greater inclusion of silver salt in the crystals which increases the total weight when the kathode is silver. Otherwise 27 and 28 should have grown heavier in the same ratio. Secondly, it is the anode solution again which is responsible.

The increase in the deposit on a silver surface indicates the existence of silver in the solution in a supersaturated state ; and this existence shows that there must be present some complex gradually dissociating, with metallic silver as one of its products. If this is the case, we should expect to find that an oxidizing environment would be capable of removing this cause of inaccuracy, while substituting another easily removed by nitric acid. As a matter of fact, Schuster and Crossly* have shown that deposits made in vacuo are heavier than when made in air ; again those made in an atmosphere of air are heavier than when made in oxygen. Of course it is understood that in all three cases the anode was only wrapped in filter paper. The solution usually contained fifteen per cent of silver nitrate, but sometimes as much as thirty per cent. They used the solution over and over again, thereby accumulating the irregular compounds. Under reduced pressure (about " $1\frac{1}{8}$ inch"), the deposits exceeded those made in air by about 0.04 per cent, while the latter exceeded those in oxygen by 0.04 per cent more. Myers,† who repeated these experiments, found the difference between deposits in air and in vacuo to be as much as 0.10 per cent for 20-40 per cent solutions.

* Proc. Roy. Soc., 50, 356 (1892).

† Wied Ann., 55, 291 ff. (1895).

In an atmosphere of nitrogen an excess of .05 per cent in the deposit was observed. Our own experiments in the same direction verify the results of these experiments, and need not be recorded here.

Putting aside for the moment the question concerning the nature of the irregular compound which can thus be partly oxidized out of existence, it seemed worth while to discover if an oxidizing agent in the solution could remove this compound to such an extent as to cause the filter paper voltameter to yield accurate results. The only practical oxidizer for this purpose is hydrogen peroxide. A fairly strong solution was prepared from pure crystalline barium peroxide and dilute sulphuric acid. The excess of acid was removed with barium hydroxide, and the solution was filtered. In this solution the usual amount of silver nitrate was dissolved, and this was used in the large bowl as well as in the lipped crucible, both anodes being wrapped in filter paper. In the large bowl black crystals of argentic peroxide, or $\text{Ag}_7\text{NO}_{11}$, were soon formed which bridged across to the kathode. While the result in the bowl thus became useless, the crucible showed no such disturbance, but yielded nevertheless a deficit of .14 per cent on comparison with a standard. This must have been due to a side reaction, especially since the kathode was found covered with small gas bubbles, which were probably oxygen. It is possible that negative electricity was carried from the kathode to the solution by the ionizing of a trace of oxygen. Better results were obtained after the hydrogen peroxide had been diluted to one-tenth its former strength; these are recorded below:—

TABLE IX.

STANDARD *vs.* FILTER PAPER VOLTAMETER CONTAINING H_2O_2 .

No. of Experiment.	Standard.	Filter paper Voltameter + H_2O_2 .	Difference.	Percentage Difference.
	grams.	grams.	milligram.	per cent.
30	1.78593	1.78648	0.55	0.031
31	1.78593	1.78642	0.49	0.027
32	1.83375	1.83406	0.31	0.017
Mean +0.025				

The usual difference of from .04 to .08 per cent is thus reduced to .025 per cent; therefore hydrogen peroxide seems to eliminate a part

of the usual disturbance. But in view of the fact that even a deficit of 0.14 per cent can be obtained, not much importance can be attached to these results, since it is impossible to say how much is due to the oxidizing action, how much to the disturbing influence capable of causing an actual deficiency.

These indirect methods of determining the presence of a complex yielding metallic silver being somewhat unsatisfactory, recourse was had to a more direct method. It seemed highly probable that the anode solution ought to be able to deposit silver without the help of the galvanic current. In order to show this, a porous cup voltameter was set up in the usual manner, except that the anode was closely wrapped in filter paper to retain the fine crystal powder which always separates from it. A current of 0.25 ampere was sent through the voltameter, and every ten minutes a portion of the clear anode solution was taken from the bottom of the porous cup by means of a small pipette, and quickly transferred to a small weighed platinum crucible.

The crucible had been previously coated with silver in order to establish equilibrium more quickly in case a compound existed in the solution which tended to deposit silver.

After one hour's standing, the liquid was removed and the crucible was washed and dried, as a deposit from electrolysis would have been. The increase in weight of the crucible must represent the deposit from the anode solution.

TABLE X.

GAIN IN WEIGHT OF SILVER IN CONTACT WITH ANODE SOLUTION.

No.	Increase in Weight. Milligram
33	0.35
34	0.08
35	0.25
36	0.63
Mean . . .	0.33

The weight of the same crucible did not change perceptibly when allowed to remain in contact with a solution of silver nitrate of like concentration, through which no current had previously been passed. The above increase in weight shows beyond a doubt, therefore, that the anode solution is capable of depositing on a silver surface either silver or some compound of this metal which must have been formed at the anode.

The most striking evidence that a compound exists around the anode which is capable of depositing pure silver is the existence of the "anode dust." This consists of a fine powder, more or less closely adhering to the anode. Examination with the microscope indicates that this powder consists of minute crystals, which have every appearance of being metallic silver. Rodger and Watson * analyzed the air-dried powder, and found as a matter of fact that the metal is essentially pure. The contrary conclusions of Myers † and others may have been based upon results obtained with small anodes, where argentic peroxide may have been formed.

In our experience the weight of this dust is approximately proportional to the area of the silver anode, with a given current. It seems highly probable, then, that the silver at first tends to separate from the anode as a polymerized ion, perhaps Ag_3^+ , according to the common principle that an unstable compound often forms the bridge between two stable conditions. ‡ The greater portion of this complex ion would be expected to break up at once into the normal argentic ion and metallic silver ($\text{Ag}_3^+ = \text{Ag}^+ + 2\text{Ag}$), the latter forming the "anode dust." The last traces of the complex might, however, persist for some time, and give rise to all the phenomena seeming to be due to the existence of supersaturated silver in the solution.

The argument has been so protracted that it is perhaps worth while to recapitulate the way in which this interpretation would explain the irregularities not to be attributed to the nitrite and oxycomplexes.

This complex ion of polymerized silver undoubtedly unloads silver at a lower potential (*i. e.* more easily) than the simple silver ion. Hence the larger the cathode surface exposed, the greater part will the complexes take in the carrying of the current, and the larger will be the deposit of silver. This consequence of the theory agrees with the experience of all experimenters. Moreover, since the complexes are unstable, and continually tending to decompose, there must be always in solution a trace of molecular unionized silver, which, being supersaturated, will deposit on contact with solid silver. If the platinum bowl has been previously lined with silver, this extra deposition will begin almost immediately; while if it has not been thus lined, an appreciable silver surface will have to be formed before the relieving of the supersaturation will begin to take place. This reasoning explains the invariable excess of the deposit upon a silver cathode over and above the amount deposited

* Phil. Trans., **186 A**, 632 (1895).

† Wied. Ann., **55**, 295 (1895).

‡ Ostwald, Z. phys. Chem., **22**, 307 (1897).

on one of platinum by the same current when only filter paper is used to protect the kathode. The results of Kahle and others seem to indicate that the presence of acid, which prevents the formation of the simple oxycomplex, is favorable to the formation of the ion Ag_3^+ . This is not surprising, since the oxycomplex is probably formed at the expense of some of the silver which would otherwise remain in the polymerized condition. The fact that the kathode deposit in the common voltameter consists of comparatively few large crystals, while the porous cup voltameter yields a host of evenly distributed small crystals, is also explained by this interpretation. Solutions having a tendency to supersaturation always tend to deposit large crystals, for obvious reasons. When the absence of acid increases the number of available hydroxyl ions, the formation of the silver-complex is less considerable; but the oxide-complexes then begin to affect the result. In concentrated solutions of the nitrate, this ion also enters into the irregularities. Thus the various irregularities are not necessarily coexistent; circumstances determine which one shall play the most important part.

There seems, then, to be concordant evidence of conflicting tendencies at work, some oxidizing and some reducing; some tending to cause the dissolving of too much silver at the anode, and some to cause the dissolving of too little. It seemed worth while to test the complicated conclusion by determining accurately the loss of weight of silver at the anode, in order to obtain a last ray of light upon the question. The disintegration of the anode renders the determination of the loss somewhat difficult; but by carefully collecting all the silver powder left in the porous cup (when no filter paper is used) on a Gooch crucible, and adding this weight to the weight of the coherent part of the anode, fairly good results may be obtained. The following table records a series of such determinations. In each case the current strength amounted to about 0.25 ampere. The experiments are arranged below in the order of current density.

In some cases the anode loses more than the ideal amount, in other cases less. Such results can only be explained by the assumption of several causes of inaccuracy, and the four which we have discussed seem capable of explaining all the changes. But it is not worth while to trace out every possible variation; enough has been said to emphasize the great complexity of the side reactions which interpenetrate a process apparently so simple, and at the same time to permit those readers who are especially interested to work out the combinations for themselves.

TABLE XI.

LOSS AT ANODE COMPARED WITH GAIN AT KATHODE.

No. of Determ.	Weight of Anode.	Loss of Anode, corrected for Silver Powder.	Deposit on Kathode.	Difference in Weight.	Percentage Difference.
	grams.	grams.	grams.	milligrams.	per cent.
37	6	2.43854	2.43744	+1.10	+0.045
38	9	2.60603	2.60420	+1.83	+0.070
39	12	3.05185	3.04996	+1.89	+0.062
40	13	1.76332	1.76283	+0.49	+0.028
41	28	2.44485	2.44599	-1.14	-0.047
42	31	2.43613	2.43744	-1.31	-0.054
43	33	2.60399	2.60420	-0.21	-0.008

In the porous cup voltameter all the anode reactions which constitute the most serious causes of inaccuracy are safely eliminated by keeping the contaminated liquid within the porous cup. It is obvious that this device, or some other accomplishing the same end, should always be used when accuracy is desired.

III. THE PURITY OF THE SILVER DEPOSIT.

An important question remains to be answered, namely, is the deposit thus obtained perfectly pure silver, or does it contain traces of included mother liquor?

That impurities in the solution, such as copper, or any of the common metals occurring with silver, do not affect silver deposit to any great extent has been shown by Lord Rayleigh. Even if the solution actually turns green from the copper dissolved at the anode, not a trace of copper can be detected in the deposit. We used on one occasion commercial silver nitrate with an anode of sterling silver wrapped in paper, and found that the difference between this and the standard was about .024 per cent, or only about .02 per cent smaller than a similar deposit with the purest silver. Metals of greater solution tension than silver have therefore no important effect on the weight of silver, although they may change the structure of the silver deposit. Of course they had always been excluded in this work.

On the other hand, the deposit, in common with most crystals, may retain small quantities of solution or wash-water. Lord Rayleigh seems to be the only one who has taken this possible source of error into account. He heated the crucibles to incipient redness, after they had been dried at 130° to 160° , and weighed. A loss of about .014 per cent was thus found. Richards and Collins, in looking for an explanation of the cause of discrepancies in the atomic weight of copper, had found by analysis the silver deposit to contain about 0.01 per cent of impurity.

For our purpose the direct method of Lord Rayleigh seemed better than the indirect analytical one. The deposits, which had been dried thoroughly at 160° and weighed, were heated over an alcohol lamp to constant weight. Care was taken to heat the whole crucible evenly, and to use as high a temperature as possible without the formation of an

TABLE XII.

LOSS OF WEIGHT OF SILVER DEPOSITS ON HEATING.

No. of Experiment.	At 150° .	At Incipient Redness.	Difference —0.10 mg.	Percentage Loss.
	grams.	grams.	milligram.	per cent.
44	1.97875	1.97859	0.06	0.003
45	1.97946	1.97907	0.29	0.015
46	1.98032	1.97998	0.24	0.012
47	1.69330	1.69284	0.36	0.021
48	1.69351	1.69307	0.34	0.020
49	1.69471	1.69411	0.50	0.030
50	2.10356	2.10326	0.20	0.010
51	2.06825	2.06764	0.51	0.025
52	2.31268	2.31234	0.24	0.010
53	2.06714	2.06663	0.41	0.020
54	1.64322	1.64266	0.46	0.028
55	1.64212	1.64166	0.36	0.022
Mean				0.018

alloy, — although several times this could not be prevented. For heating the deposits on platinum gauze (see Table IX), a small oven was constructed from a large porcelain crucible, covered by a platinum funnel. The platinum disc was supported by a wire reaching through the tube of the funnel. In this case, the silver in the platinum crucibles with which that on the gauze was to be compared, was heated in the oven also, in order to expose both to the same temperature. Since the figures of this comparison are given in Table IX, it is necessary only to tabulate here the loss observed in crucibles when heated directly. Of course allowance has been made for the very slight hygroscopic loss (0.10 milligram) which a platinum crucible without silver deposit would have undergone. The silver films were usually those remaining from some of the preceding determinations.

This percentage loss is slightly higher than that given by Lord Rayleigh, and still larger than that determined indirectly by Richards and Collins. It is evident that the amount of included mother liquor varies according to the rate and mode of deposition, and it is quite possible that different average amounts were really included in the several investigations. The inclusion is probably chiefly in recesses in the platinum cathode. The differences in included liquid given in the above table are of the same order as the differences in the uncorrected weights of silver given at first; * hence we may ascribe at least a part of the differences in the early table to inclusion of mother liquor.

All this evidence unites in indicating that even under the best conditions the silver does not exceed a purity of 99.99 per cent; and in applying a correction, one should obviously use the value found in the particular investigation under review.

IV. THE ATOMIC WEIGHT OF COPPER.

Having thus clear light upon the various errors of the silver voltameter, it became a matter of great interest to recur to the original question which started the whole investigation, namely, the quantitative accuracy of Faraday's law.

Accordingly, a voltameter like that used by Richards and Collins † — a modified form of Lord Rayleigh's instrument — was compared with a standard porous cup voltameter, neither precipitate being ignited. The

* See page 418.

† These Proceedings, **35**, 133 (1899).

eighteen results, including three given in the last paper, are recorded below : —

TABLE XIII.

COMPARISON OF POROUS CUP WITH MODIFIED LORD RAYLEIGH VOLTAMETER.

No. of Experiment.	Current Strength.	Weight Ag in Standard (Porous Cup).	Weight Ag in Filter Paper Voltameter.	Difference.	Percentage Difference.
	amperes.	grams.	grams.	milligrams.	per cent.
A. 37		1.94124	1.94267	1.43	+0.074
A. 38		1.76283	1.76425	1.42	+0.080
A. 39		3.04996	3.05270	2.74	+0.090
56	0.25	2.26624	2.26680	0.56	+0.024
57	0.25	2.17289	2.17215	0.26	+0.012
58	0.25	2.17896	2.18071	1.75	+0.080
59	0.25	2.11095	2.11134	0.39	+0.019
60	0.25	2.14906	2.14974	0.68	+0.032
61	0.25	2.09580	2.09648	0.68	+0.033
62	0.25	2.09580	2.09650	0.70	+0.033
63	0.25	1.65487	1.65520	0.33	+0.020
64	0.25	2.09756	2.09840	0.84	+0.040
65	0.25	2.09756	2.09834	0.78	+0.037
66	0.25	2.02063	2.02100	0.37	+0.018
67	1.25	2.02063	2.02144	0.81	+0.040
68	0.45	2.31490	2.31568	0.78	+0.034
69	0.12	2.22259	2.22343	0.84	+0.038
70	1.00	2.67266	2.67364	0.98	+0.037
Mean					+0.041

The comparison of the deposits thus shows that when the anode is wrapped in paper, the deposit is on the average greater by 0.041 per cent. This average difference is smaller than that given in the previous paper, but it is probably more accurate, because it comprehends so many deter-

minations. The wide deviations between the individual determinations illustrate the uncertainty of a voltameter in which the anode is merely wrapped in filter paper.

When to this difference is added the amount (0.018 per cent) caused by the included mother liquor, it is obvious that the weight of silver observed in the experiments upon Faraday's law made by Richards and Collins must have been 0.059 per cent too heavy. This would cause the observed electro-chemical atomic weight of copper (63.563 *) to be too small by the same percentage. Correcting for this error, the atomic weight of copper calculated from the results of the experiments upon Faraday's law becomes 63.601, while the most probable value found in purely chemical ways is 63.604. †

The agreement is as close as the probable accuracy of the electrolytic determinations. Thus good experimental evidence is furnished, showing that Faraday's law holds rigorously true in aqueous solution at ordinary temperatures. Apparent deviations are simply due to the disturbing effect of side reactions.

V. THE ELECTROCHEMICAL EQUIVALENT OF SILVER.

It becomes now an important matter to determine, if possible, a correction which might be applied to the methods of earlier physical experiments upon the electrochemical equivalent of the ampere. Such correction must at best be an unsatisfactory expedient; the only really satisfactory method of proceeding would be to repeat the work wholly, using the new voltameter as a chemical measure of the current. But such a proceeding involves an expenditure of time not now at our disposal; hence it seems not wholly fruitless to attempt the correction of the older results.

The series of comparisons of the standard with the filter paper voltameter just given (p. 422) will hardly serve for the purpose, since the latter voltameter changes in its indications with every change of form; and the two comparisons with Lord Rayleigh's form, given in the previous paper, form too small a basis upon which to make so serious a correction. Hence another series of these experiments was made, in which the porous cup voltameter was compared directly with a voltameter

* This result was obtained by extrapolation for a copper kathode of zero area. It had a "probable error" of 0.004, and possibly contained a source of error tending to make it slightly too large.

† Richards, *These Proceedings*, **26**, 293 (1891).

made exactly according to Lord Rayleigh's directions. These are given below, together with the two determinations given in the last paper.

TABLE XIV.

COMPARISON OF POROUS CUP WITH ORIGINAL RAYLEIGH VOLTAMETER.

No. of Experiment.	Weight of Silver in Standard.	Weight of Silver in Lord Rayleigh's Form.	Difference.	Percentage Difference.
	grams.	grams.	milligrams.	per cent.
A. 40	3.09629	3.09918	2.89	+0.093
A. 41	2.53256	2.53439	1.83	+0.072
71	2.16129	2.16538	1.09	+0.050
72	2.09580	2.09653	0.73	+0.035
73	1.65487	1.65549	0.62	+0.038
Mean				+0.058

This is 0.017 per cent more than the average of the preceding series. Probably a mean of the average of the two series, or +0.050 per cent, represents as nearly as possible the correction to be applied to Lord Rayleigh's voltameter. This value is not only an average of averages, involving twenty-three determinations, but is also very nearly the mean between the two extreme results 0.012 and 0.093. It may probably be relied upon to within 0.01 per cent of the total weight of the silver.

It finds support in some results given in Kahle's* paper. He made a comparison between an ordinary voltameter and one in which the anode solution was constantly siphoned off and thus prevented, more or less perfectly, from reaching the kathode. The solution in both voltameters was strongly acid, but equally so. The siphon voltameter deposited, in good agreement with the above results, 0.05 per cent less silver than the ordinary voltameter.

The fact, however, that the extremes vary from .012 per cent to .093 per cent indicates that unless great care is taken in the way in which the anode is wrapped, in the strength of the current and in the size of the anode, the depositions in the ordinary voltameter according to Lord Rayleigh are untrustworthy.

* Wied. Ann. N. F., 67, 30 (1899).

In order to correct Patterson and Guthe's results, it became necessary to repeat comparisons of the standard with the voltmeter containing old solution saturated with oxide, as used by them.

TABLE XV.

STANDARD *vs.* PATTERSON AND GUTHE'S METHOD.

No. of Experiment.	Date.	Amp.	Weight of Silver in Standard.	Weight of Silver in P. & G.	Difference.	Percentage Difference.
			grams.	grams.	milligrams.	per cent.
A. 43	6-11-99		1.89800	1.90238	4.38	0.230
A. 44	6-18-99		2.55012	2.55460	4.48	0.176
74	3- 6-01	0.25	2.08330	2.08492	1.62	0.078
75	3-14-01	0.25	2.09756	2.09951	1.95	0.094
76	3-27-01	0.25	2.02063	2.02217	1.54	0.077
77	4- 1-01	0.45	2.31490	2.31734	2.44	0.106
78	4- 4-01	0.12	2.22259	2.22344	0.85	0.039
79	5- 8-01	1.00	2.67266	2.67527	2.61	0.098
Mean						0.112

This result is perplexing, and much lower than the average computed from the first two determinations, which was given in the preceding paper. It indicates that the Patterson and Guthe method gives results 0.06 per cent higher than those given by Lord Rayleigh's method, while Patterson and Guthe's own comparisons give a difference of 0.11 per cent.* Evidently the saturated-oxide method is more variable in different hands even than Lord Rayleigh's. Perhaps the safest number to use in the correction is the average of both, 0.085 per cent above the Lord Rayleigh method, or 0.135 per cent above the porous cup method.

We are now in a position to make an approximate correction for the effect of the contaminating anode liquid in each of the more important investigations which bear upon the electro-chemical equivalent of silver. Of these, those of Lord Rayleigh, Fr. and W. Kohlrausch, K. Kahle,

* Phys. Review, **7**, 280. Kahle (Wied. Ann. **67**, 32, also Brit. Ass't. A. Sc. 1892, 148), found 0.05 per cent, but his solutions were probably fresher.

and Patterson and Guthe have attracted most attention. Since the first three investigations used a voltmeter of the original Lord Rayleigh type, a correction of -0.05 per cent should be applied to each. Moreover, Kohlrausch and Kahle did not heat their deposits to redness; hence an additional reduction of about 0.016 per cent* is necessary. Finally, Kohlrausch deposited the silver on a silver kathode, while Lord Rayleigh and Kahle made their determinations with platinum kathodes — a correction which leads to a further reduction of $.01$ per cent for Kohlrausch's value, or 0.076 in all. Patterson and Guthe, on the other hand, deposited the silver on platinum, but used old solutions saturated with silver oxide. Such solutions may have yielded about 0.135 more silver than the standard. When the correction for heating is added to this the total reduction becomes 0.15 per cent. Thus we are led to the following table: —

TABLE XVI.

THE CORRECTED ELECTROCHEMICAL EQUIVALENT OF SILVER.

(1) Lord Rayleigh and Mrs. Sidgwick,†	0.0011179	-0.050%	0.0011173
(2) Fr. & W. Kohlrausch,‡	0.0011183	-0.076	0.0011175
(3) Kahle,§	0.0011183	-0.066	0.0011176
(4) Patterson & Guthe,	0.0011192	-0.150	0.0011175
Average			0.0011175

The greatest deviation from this average is 0.02 per cent, a remarkable agreement considering the variety of physical method used by the experimenters. Lord Rayleigh and Kahle used an electro-dynamometer and Kohlrausch an accurate tangent galvanometer for the calculation of the current, while Patterson and Guthe made themselves entirely free from the acceleration of gravity or the strength of the magnetic field by means of an absolute electro-dynamometer. Hence for the present the great bulk of evidence seems to favor the value 0.0011175 , the mean of four entirely independent determinations, as the true electrochemical equivalent of silver. Our data also give the electrochemical equivalent of copper in the cupric condition as 0.00032929 gram per ampere per second.

The number of coulombs attached to one gram equivalent of any electrolyte is therefore $96,580$.

* The average of Lord Rayleigh's results and ours.

† Phil. Trans., **175**, 411 (1884).

‡ Wied. Ann. N. F., **27**, p. 1 (1886).

§ Wied. Ann. N. F., **67**, 1 (1899).

|| Phys. Review, **7**, 257 (1898).

A few more points may be touched upon here, which follow directly from the new value of the equivalent. A great number of physical instruments have been standardized on the basis of a somewhat higher electrochemical equivalent of silver, 0.001118. Will they be affected by the lowering of this number? Evidently not, since if the value corresponding to a given mode of deposition is applied throughout, whenever this method is used, no constant error can result. Thus our low value cannot be employed when the anode is unprotected, and the deposit not heated to redness.

Therefore, as was shown in our last paper, the discovery of a constant error in the silver voltameter cannot help the discrepancy which exists between the electrical and mechanical methods of determining Joule's equivalent.

It is to be hoped that in the future, however, all experimenters will use some method, such as ours, in which the anode complications are excluded. Obviously even the present condition of electrical science demands a more precise electrochemical definition of the ampere than that now prescribed.

The present research seems to define the practical unit of current strength no less accurately than the practical unit of electro-motive force has been defined. Thus in a laboratory provided with pure chemicals, each of these units may be established without outside help, and with their assistance a standard ohm may be produced without comparison with any other standard ohm.

VI. SUMMARY.

The results of the prolonged investigation may be summed up as follows:—

1. The electrochemical equivalent of silver as determined by the Lord Rayleigh voltameter is too high by at least 0.05 per cent.
2. The true rate of deionization of silver can be determined by the use of a porous cup which prevents the solution at the anode from reaching the kathode. Results of great consistency and accuracy are then obtainable.
3. The porous cup does not introduce any new source of error, for without it the same low results may be obtained when the anode is placed below the kathode.
4. At higher temperature the complications grow larger.
5. The main disturbing factor is a complex silver ion formed at the anode and carried over to the kathode, where it decomposes, thereby

increasing the deposit of silver. Most of this polymerized material decomposes at once, however, forming the silver dust at the anode.

6. The hydroxyl ion discharges at the anode, forming silver oxide and probably so-called peroxide. Ionized hydrogen is thus developed.

7. Dissolved gases affect the deposit whenever they react with the complex ions.

8. Nitrite is formed at the anode, but has probably not much effect on the weight of the deposit.

9. The deposited silver always contains included solution, varying in amount from 0.01 per cent to 0.04 per cent according to circumstances.

10. A new name, *coulometer*, is proposed, to replace the old and unsuitable designation *voltameter*.

11. The true electrochemical equivalent of silver is probably 0.0011175 milligram per coulomb.

12. Therefore, 96580 coulombs are associated with one gram equivalent of any electrolyte.

13. The electrochemical equivalent of cupric copper is 0.00032929; therefore the electrochemical atomic weight of copper (63.601) is in close agreement with the chemical value (63.604).

14. Faraday's law is thus verified for two kathions more exactly than ever before.

CAMBRIDGE, MASS., U. S. A.